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Abstract

The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and L-phenylalanine, in the presence of piperidine, when reacted with copper sulfate pentahydrate, forms a polymeric square pyramidal five-coordinate copper complex, [Cu(C₁₇H₁₄O₃)(C₄H₁₀N₂)]. The axial position of the square pyramid is occupied by the carboxyl O atoms of a neighboring molecule.

Keywords

n, salicylidene, phenylalaninato, kn, piperidine, ii, k³, copper

Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

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(Piperidine- κN)[*N*-(salicylidene)phenylalaninato- $\kappa^3 O, N, O'$]copper(II)**Ray J. Butcher,^{a*} Garry M. Mockler^b and Owen McKern^b**^aDepartment of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, and ^bDepartment of Chemistry, University of Wollongong, NSW 2522, Australia

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Key indicators

Single-crystal X-ray study

T = 293 KMean $\sigma(C-C)$ = 0.005 Å*R* factor = 0.036*wR* factor = 0.082

Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and L-phenylalanine, in the presence of piperidine, when reacted with copper sulfate pentahydrate, forms a polymeric square pyramidal five-coordinate copper complex, $[Cu(C_{17}H_{14}O_3)(C_4H_{10}N_2)]$. The axial position of the square pyramid is occupied by the carboxyl O atoms of a neighboring molecule.

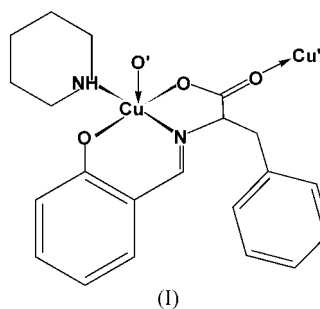
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Comment

Galactose oxidase is a type II copper protein that catalyses the oxidation of primary alcohols to aldehydes with a concomitant reduction of molecular oxygen (Whittaker, 1994). Its crystal structure (Ito *et al.*, 1994) reveals a unique mononuclear Cu site with two N donors (from histidine imidazole groups), two O donors (one axial and one equatorial tyrosine group), and an exogenous water or acetate molecule, all arranged in a distorted square-pyramidal coordination. Several different theories have been proposed to explain how galactose oxidase, which contains a single Cu atom, can catalyse a two-electron redox reaction. The currently accepted theory (Whittaker & Whittaker, 2001) suggests that the 'inactive' form of galactose oxidase is oxidized by the loss of one electron to produce the 'active' form, which contains a tyrosine (tyrosine 272) free radical ion coupled to the Cu^{II} ion. The active form is then reduced to the Cu^I species and the alcohol oxidized to the corresponding aldehyde.



There has been considerable interest in the study of model compounds of galactose oxidase in recent years (Butcher *et al.*, 2003*a,b*; Kruse *et al.*, 2002; Shimazaki *et al.*, 2002; Thomas *et al.*, 2002). One group of compounds that has attracted considerable interest consists of five-coordinate copper complexes with tridentate Schiff base ligands derived from the condensation of amino acids with substituted salicylaldehydes. In this type of complex, the Cu coordination sphere also contains a monodentate Lewis base. With two exceptions (Plesch *et al.*, 1997; Sivy *et al.*, 1994), X-ray crystallographic studies have shown that these Cu^{II} compounds contain Cu^{II} in a distorted square-

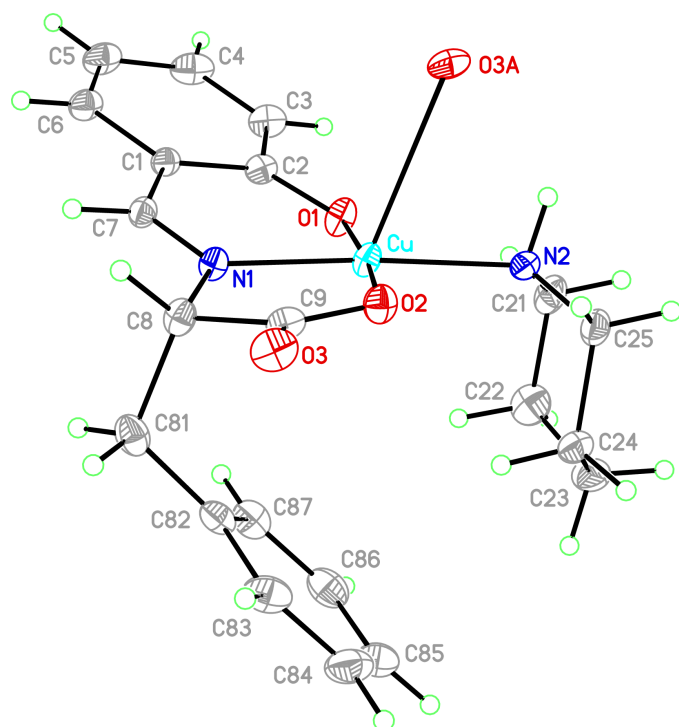


Figure 1
View of the coordination sphere of the Cu, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size.

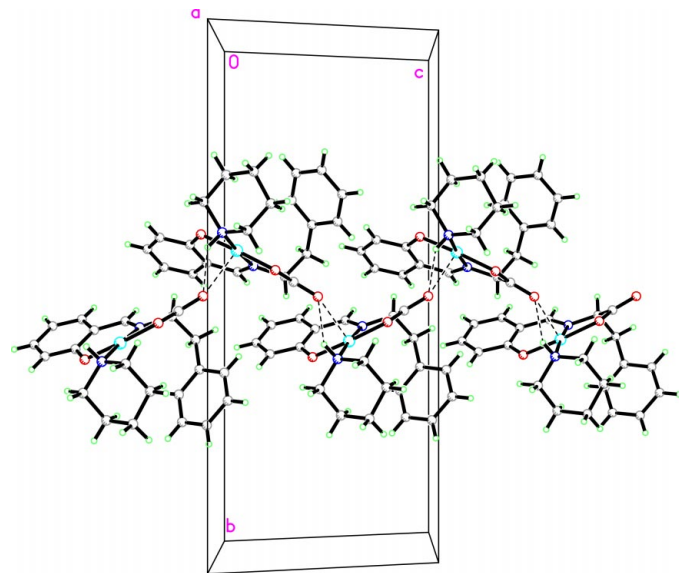


Figure 2
The molecular packing viewed along the *a* axis, showing the zigzag chain of complexes in the *c* direction, linked through the carboxyl O atoms.

pyramidal environment and fit into three main types:

(i) monomeric with a water molecule occupying the fifth coordination site (Butcher *et al.*, 2003a; Dawes *et al.*, 1982; Fujimaki *et al.*, 1971; Garcia-Raso *et al.*, 1996; Korhonen & Hamalainen, 1979; Ueki *et al.*, 1969; Warda *et al.*, 1996; Warda, 1997g; Warda, 1998a,d,e,f);

(ii) dimeric with an adjacent phenolic O atom occupying the fifth coordination site (Butcher *et al.*, 2003b; Davies, 1984; Hamalainen *et al.*, 1978; Hill & Warda, 1999; Warda, 1997a,e; Warda, 1998b,c,e,g; Warda, 1999; Warda *et al.*, 1998);

(iii) polymeric with the fifth coordination site occupied by an adjacent carboxyl O atom (Ueki *et al.*, 1967; Kettman *et al.*, 1993; Korhonen *et al.*, 1984; Plesch *et al.*, 1998; Warda *et al.*, 1997; Warda, 1997a,b,c,d,f; Sivy *et al.*, 1990).

The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and L-phenylalanine, in the presence of piperidine, forms a square-pyramidal five-coordinate Cu complex, (I), of type iii. In this complex, the carboxyl O from an adjacent molecule occupies the apical site, at a distance of 2.674 (2) Å, forming a polymeric zigzag chain in the *c* direction. Unlike other square-pyramidal five-coordinate analogs, in this example, the Cu is only slightly displaced [0.012 (1) Å] from the basal plane formed by atoms O1, O2, N1, and N2, due to the comparatively weak out-of-plane bond to a neighboring carbonyl O donor. Neither the Cu—O1, Cu—O2, and Cu—N1 bond distances [1.918 (2), 1.964 (2), and 1.935 (2) Å, respectively] nor the Cu—N2 bond distance [2.002 (3) Å] differ significantly from those of similar type iii polymeric compounds mentioned above.

Experimental

The title complex was synthesized in two stages. In the first stage, 10 g of L-phenylalanine (phenala) and an equimolar amount of sodium hydroxide were dissolved in 300 ml of hot water. To this solution was added an equimolar quantity of copper sulfate pentahydrate dissolved in 100 ml of water. The blue–purple $[\text{Cu}(\text{phenala})_2] \cdot n\text{H}_2\text{O}$ compound precipitated on cooling the solution. 6 g of this compound, two mole equivalents of salicylaldehyde, triethylamine (10 ml) and piperidine (10 ml) were refluxed in methanol for 1 h. The hot solution was filtered and allowed to stand until the dark green product precipitated from solution. X-ray quality crystals were grown by slow evaporation from a methanol–acetonitrile solution.

Crystal data

$[\text{Cu}(\text{C}_{17}\text{H}_{14}\text{O}_3)(\text{C}_4\text{H}_{10}\text{N}_2)]$
 $M_r = 415.96$
 Monoclinic, *Cc*
 $a = 8.7002$ (9) Å
 $b = 22.6624$ (15) Å
 $c = 9.9711$ (8) Å
 $\beta = 106.010$ (7)°
 $V = 1889.7$ (3) Å³
 $Z = 4$

$D_x = 1.462$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 72 reflections
 $\theta = 5.3$ – 14.0°
 $\mu = 1.18$ mm^{−1}
 $T = 293$ (2) K
 Chunk, dark green
 0.58 × 0.28 × 0.20 mm

Data collection

Siemens P4S diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.338$, $T_{\max} = 0.475$
 3692 measured reflections
 3609 independent reflections
 2912 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.000$
 $\theta_{\max} = 32.5^\circ$
 $h = -13 \rightarrow 0$
 $k = 0 \rightarrow 34$
 $l = -14 \rightarrow 15$
 3 standard reflections every 97 reflections
 intensity decay: 1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.082$	$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$
$S = 1.02$	Extinction correction: <i>SHELXL</i>
3609 reflections	Extinction coefficient: 0.0019 (5)
245 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	180 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2$	Flack parameter = -0.001 (13)
$+ 0.1576P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu—O1	1.918 (2)	Cu—N2	2.022 (3)
Cu—N1	1.935 (2)	Cu—O3A	2.674 (2)
Cu—O2	1.964 (2)		
O1—Cu—N1	91.49 (10)	O2—Cu—N2	94.24 (11)
O1—Cu—O2	173.91 (10)	O3A—Cu—O1	92.3 (1)
N1—Cu—O2	82.65 (10)	O3A—Cu—O2	88.1 (1)
O1—Cu—N2	91.69 (11)	O3A—Cu—N1	109.7 (1)
N1—Cu—N2	175.76 (11)	O3A—Cu—N2	73.0 (1)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots O3 ⁱ	0.91	2.24	2.841 (4)	123

Symmetry code: (i) $x, 2 - y, z - \frac{1}{2}$.

All H atoms were included in calculated positions with C—H distances ranging from 0.93 to 0.98 \AA and N—H distances of 0.91 \AA . The H atoms were then included in the refinement using a riding-motion approximation, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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